Journal of Molecular Catalysis A: Chemical 307 (2009) 9–12

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Protophilic amide ionic liquid assisted esterification and catalysis mechanism

Fei Xu, Hongyu Chen, Haibo Zhang, Xiaohai Zhou*, Gongzhen Cheng*

College of Chemistry, Wuhan University, Wuhan 430072, PR China

ARTICLE INFO

Article history:
Received 3 February 2008
Received in revised form 2 March 2009
Accepted 7 March 2009
Available online 20 March 2009

Keywords:
Protophilic amide
Brønsted acidic ionic liquid
Esterification
Mechanism

ABSTRACT

Esterification of alcohols by acetic acid has been carried out at room temperature in a group of Brønsted acidic ionic liquids derived from protophilic amides. Good conversion ratio and excellent reaction rate are obtained, and the liquid esters formed a separate phase that is decanted without containing ionic liquid in it. The possible reason of faster and more efficient esterification is: by stabilizing the protonated acetic acid and limiting the alcohol protonation, protophilic amide ionic liquid (PAIL) accelerates the reaction.

1. Introduction

It is well known that organic esters are indispensable products or intermediates in chemical industry [1]. Among all the catalysts of esterification, liquid inorganic acids are most important and have the longest history [2]. However, many drawbacks of this traditional method have shown up: Firstly, removal of water or/and use of an excess amount of the reactants is needed to attain satisfactory conversion [3]. Furthermore, the removal of the liquid inorganic acid or the separation of the product from the catalyst also calls for a large effort, and pollution may be produced if a large amount of volatile organic solvents and liquid inorganic acid are used [4].

As a kind of green reaction media, ionic liquids (ILs) offer many advantages from the environmental perspective since it has been used in many chemical reactions [5–10]. It is also reported that esterification can be carried out in these non-flammable, thermally stable, non-volatile, and recyclable solvents [11–17]. Although elegant work has been done in this area, some problems still exist. For example, how to collect the ester easily from the reaction liquid, how to purify the product which contains ionic liquid in it, and the cost problem, all these have limited the application of the ILs.

Although one kind of protophilic amide ionic liquid (PAIL) had already been used for esterification [17], in this paper, we broadened the scope of PAIL (Scheme 1) [18], and used them for esterification of ethanol and butanol by acetic acids (Scheme 2). During our work, we were surprised to find that ALL kinds of ILs derived from protophilic amides can be used as excellent catalysts for esterification. The most valuable merits of PAIL are described as follows: (1) compared to sulfuric acid, they show a high catalytic activity, (2) the ester synthesized in the ionic liquids can form a different phase, which makes it convenient to separate the product from the reaction phase, (3) ^{1}H NMR shows that there is not any ionic liquid dissolved in the product, in other words, it is much easier to purify the raw ester. Furthermore, we used ^{13}C NMR to investigate the catalysis mechanism and found that there are some differences between the esterifications catalyzed by strong inorganic acid and by PAIL. According to the ^{13}C NMR results, its unique catalytic mechanism and high catalytic activity may result from the special structure of PAIL.

2. Experimental

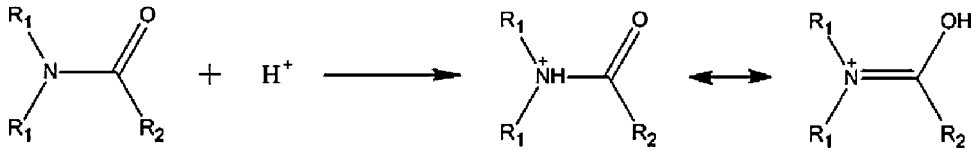
2.1. General remarks

All commercial chemicals were used as received. The reactions were carried out in a round-bottom flask with a stirrer. The reacting acids and alcohols were added to PAILs. The esterification reactions proceed for a period of time ranging from 4 to 10 h with vigorous stirring at room temperature. After the reaction, the ester and ionic liquid were separated conveniently by decanting. The products were analyzed by Varian Mercury VX-300M NMR, and the conversion rate was calculated from the ester and the remaining alcohol.

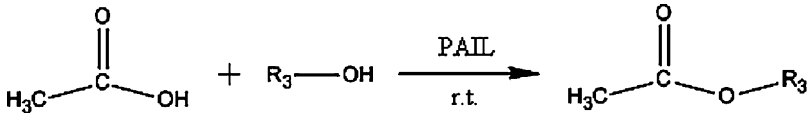
All NMR measurements were carried out in this way: the compounds were sealed in capillaries and put into the NMR tubes containing $CDCl_3$ as the internal reference and locking solvent.

* Corresponding authors. Tel.: +86 13986014216; fax: +86 68754067.
E-mail address: zxh7954@hotmail.com (X. Zhou).

1381-1169/$ – see front matter.
doi:10.1016/j.molcata.2009.03.003



Scheme 1. The resonance structure of PAIL.



Scheme 2. Esterification catalyzed by PAIL (R_3 = ethyl, butyl).

2.2. Synthesis of PAIL

The preparation of PAIL was as follows [17,18]:

20.0 g of sulfuric acid or 19.2 g of methyl sulfonic acid (0.2 mol) was added to a 100 mL flask containing equivalent protophilic amide (0.2 mol), and the mixture was stirred for 12 h at room temperature. The following protophilic amide had been used in this paper: N,N-dimethylformamide (DMF); acetamide (A); N,N-dimethylacetamide (DMA); succinimide (S); N-methyl-2-pyrrolidonium (NMP).

2.3. Typical esterification procedure

14.8 g of 1-butanol or 9.2 g of ethanol (0.2 mol), 12 g acetic acid (0.2 mol) and PAIL (0.1 mol) were added to a 200 mL flask with a stirrer. The reaction mixture was stirred for 4 h at room temperature. Reaction progress was monitored by ^{1}H NMR. After the reaction, the ester was isolated by decantation.

3. Results and discussions

3.1. Catalysis of esterification

Our initial efforts were directed toward investigating the formation of ethyl acetate and butyl acetate catalyzed by $[A]^+HSO_4^-$ or $[A]^+CH_3SO_3^-$. The results of experiments are summarized in Tables 1 and 2. It is obvious that PAIL was very efficient in esterification. Excellent conversions were obtained in all the cases at room temperature. The best reaction time was ca. 4 h, and the best ratio of Acid/alcohol/IL was 2:2:1. For the purpose of comparison, the same esterification reaction was also carried out with equivalent concentrated sulfuric acid (98%, 4.9 g) as catalyst (Table 1, entry 9 and Table 2, entry 9). It was apparent that the catalytic performance of PAIL (Table 1, entries 1–8 and Table 2, entries 1–8) is much better than that of the concentrated sulfuric acid (Table 1, entry 9 and Table 2, entry 9) under the same reaction conditions, both in conversion ratio and reaction rate. There is no doubt that the IL of $[A]^+HSO_4^-$ and $[A]^+CH_3SO_3^-$ are superior catalysts of esterification.

We used other protophilic amides to synthesize PAILs with sulfuric acid or methyl sulfonic acid, and catalyzed esterification. The results were shown in Table 3. We found that ALL the PAILs showed a high catalytic activity for esterification. All conversion ratios were above 88%, which was satisfactory. Moreover, the esters formed another phase in most systems and could be easily separated from the synthesis mixture. It is noteworthy that ^{1}H NMR showed some products contained little PAIL, which makes this kind of method even more useful. Among all PAILs, $[A]^+HSO_4^-$ and $[DMF]^+HSO_4^-$ have the highest catalytic activity, and the esters from these two are of the highest purity.

3.2. Esterification mechanism

It is well-known that the classical esterification mechanism (Scheme 3) has two key steps; one is the protonation of acetic acid, and the other is the nucleophilic attack of the protonated acetic acid by the alcohol. The performance of PAIL brought the questions why PAIL is such an excellent catalyst for esterification and what is the difference between the esterification catalyzed by inorganic acid and PAIL? To investigate the mechanism of the reaction, we measured the ^{13}C NMR of acetic acid and PAIL, and the results were summarized in Table 4.

As shown in Table 4, the chemical shift of carbon on the carbonyl of acetic acid increased as the inorganic acid was added to acetic acid (Entry 1 to 3). On the other hand, when PAIL was added into acetic acid, dramatic change in chemical shift was not found, which indicates a very small change in electron density (Entry 1, 7, 8). Furthermore, the electron density of DMF in the mixture of acetic acid and $[DMF]^+HSO_4^-$ ($[DMF]^+CH_3SO_3^-$) was lower than that of pure DMF (Entry 4, 7, 8), but higher than that of pure $[DMF]^+HSO_4^-$ ($[DMF]^+CH_3SO_3^-$) (Entry 4 to 6). Inorganic acids such as sulfuric

Table 1
Results of esterification of ethyl acetate under different conditions[a].

Entry	Catalyst	Acid/ethanol/IL (mol/mol)	Conversion (%)	Temperature (°C)	Time (h)
1	$[A]^+HSO_4^-$	1:1:1	98	r.t.	4
2		2:2:1	95	r.t.	4
3		4:4:1	85	r.t.	4
4		4:4:1	90	r.t.	10
5	$[A]^+CH_3SO_3^-$	1:1:1	93	r.t.	4
6		2:2:1	92	r.t.	4
7		4:4:1	84	r.t.	4
8		4:4:1	85	r.t.	10
9	H_2SO_4	4:4:1	74	r.t.	24

[a] Conversion rate are based on ^{1}H NMR, no unreacted substrate and product in IL phase were detected by ^{1}H NMR.

Table 2
Results of esterification of butyl acetate under different conditions[a].

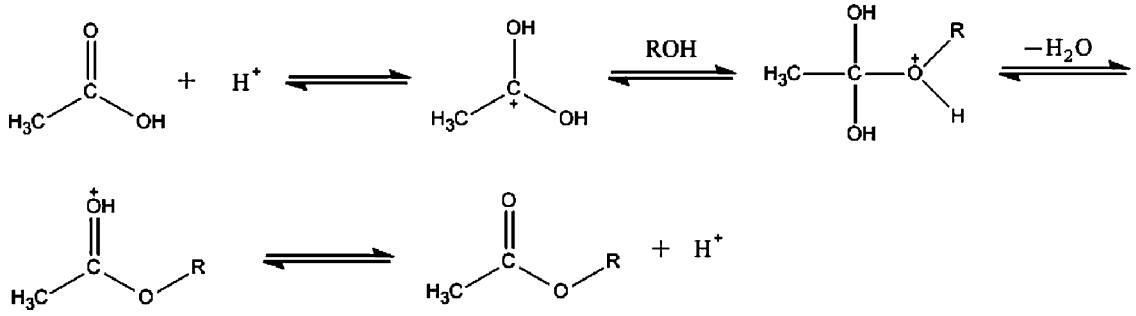
Entry	Catalyst	Acid/Butanol/IL (mol/mol)	Conversion (%)	Temperature (°C)	Time (h)
1	$[A]^+HSO_4^-$	1:1:1	96	r.t.	4
2		2:2:1	93	r.t.	4
3		4:4:1	84	r.t.	4
4		4:4:1	87	r.t.	10
5	$[A]^+CH_3SO_3^-$	1:1:1	94	r.t.	4
6		2:2:1	90	r.t.	4
7		4:4:1	83	r.t.	4
8		4:4:1	87	r.t.	10
9	H_2SO_4	4:4:1	70[b]	100	4

[a] Conversion rate are based on ^{1}H NMR, no unreacted substrate and product in IL phase were detected by ^{1}H NMR.
[b] Ref. [18].

Table 3
Results of esterification for ethyl acetate and butyl acetate in different catalysts[a].

Entry	Catalyst	Ethyl acetate		Butyl acetate	
		Conversion (%)	Layer separation	Conversion (%)	Layer separation
1	$[A]^+ HSO_4^-$	95	√	93	√
2	$[A]^+ CH_3SO_3^-$	92	√	89	√
3	$[DMF]^+HSO_4^-$	95	√	93	√
4	$[DMF]^+CH_3SO_3^-$	88	√	91	√
5	$[DMA]^+HSO_4^-$	91	√	87	√
6	$[DMA]^+CH_3SO_3^-$	88	√	88	√
7	$[S]^+HSO_4^-$[c]		×	92	√
8	$[S]^+CH_3SO_3^-$[c]		×	94	√
9	$[NMP]^+CH_3SO_3^-$[c]		×	95[b]	√

[a] Conversion rate are based on ^{1}H NMR. All reactions are carried out at r.t., lasting for 4 h, and the ratio of acid/alcohol/IL is 2:2:1.
[b] The result of $[NMP]^+CH_3SO_3^-$ is cited [18], and the ratio of acid/alcohol/IL is 4:4:1.
[c] The esters cannot form another phase in these systems, so the results are not given out for their low purity.

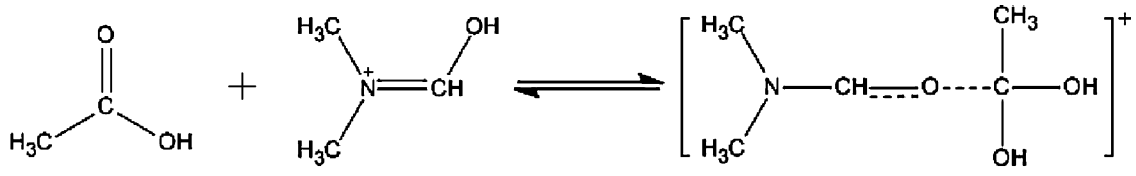


Scheme 3. The classical esterification mechanism.

Table 4
Chemical shifts for ^{13}C NMR of acetic acid, DMF and PAIL[a].

Entry	Sample	CH_3COOH		DMF		
		CH_3	CO	CH_3	CH_3'	CO
1	CH_3COOH	15.712	173.395	–	–	–
2	$CH_3COOH + H_2SO_4$	15.882	178.824			
3	$CH_3COOH + CH_3SO_3H$	16.061	175.179	–	–	–
4	DMF	–	–	26.332	31.454	158.230
5	$[DMF]^+HSO_4^-$			34.876	40.648	165.100
6	$[DMF]^+CH_3SO_3^-$			34.014	39.724	165.715
7	$CH_3COOH + [DMF]^+HSO_4^-$	16.077	172.394	30.148	35.958	160.621
8	$CH_3COOH + [DMF]^+CH_3SO_3^-$	16.199	170.563	29.590	35.307	161.012

[a] The ratio of acetic acid/catalyst is 2:1.

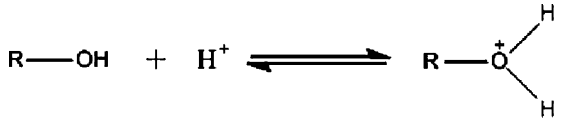


Scheme 4. Acetic acid attacked by $[DMF]^+$.

Table 5
Chemical shifts for ^{13}C NMR of ethanol and butanol in different catalysts[a].

Entry	Catalysts	CH_3CH_2OH			$CH_3CH_2CH_2CH_2OH$		
		β-CH_3	α-CH_2	δ-CH_3	γ-CH_2	β-CH_2	α-CH_2
1	–	13.458	52.849	9.305	14.758	30.521	57.175
2	H_2SO_4[b]	11.322	55.782[c]		–	–	–
3	CH_3SO_3H	12.158	54.561	9.161	14.383	28.904	58.328
5	$[DMF]^+HSO_4^-$[b]	12.709	53.605	9.192	14.500	29.425	57.668
6	$[DMF]^+CH_3SO_3^-$	13.355	53.112	9.348	14.649	30.139	57.337

[a] The ratio of alcohol/catalyst is 2:1.
[b] The alcohol in H_2SO_4 had been dehydrated to form aether more or less, so we only used the peak of ethanol.
[c] Butanol was dehydrated so much that the result is not given out.



Scheme 5. The protonation of alcohol.

acid and methyl sulfonic acid could protonate the carbonyl of acetic acid (Scheme 3); obviously, the change on ^{13}C NMR is the result of the protonation of the carbonyl (Entry 1 to 3). However, in PAIL, we assumed the acetic acid was not protonated by H^+, but attacked by $[DMF]^+$ (Scheme 4). The carbonyl of DMF shared its electron with the protonated carbonyl of acetic acid, making its electron density higher than that of the protonated carbonyl in inorganic acid. Because a new intermediate is formed between acetic acid and $[DMF]^+$ (Scheme 4), the electron density of DMF in the intermediate should be between pure DMF and $[DMF]^+HSO_4^-$ ($[DMF]^+CH_3SO_3^-$). The assumption above agrees with the results in Table 4. By sharing its electron cloud with protonated carbonyl, PAIL stabilized the reaction intermediate, protonated acetic acid, and made the reaction easier to proceed.

Besides the influence on protonated carbonyl of acetic acid, we also investigated the effect of PAIL on alcohol. The ^{13}C NMR of ethanol and butanol in inorganic acid or PAIL was listed in Table 5. The chemical shift of carbon on alcohol increased after adding inorganic acid (Entry 1 to 3), especially α carbon. When PAIL was added, we found only a slight increase of chemical shift, which indicates a much smaller decrease of electron density (Entry 1, 5, 6). This observation indicates that the alcohol was protonated differently in different environment (Scheme 5). Since the protonated alcohol had lower electron density on oxygen, it was more difficult for it to attack the protonated carbonyl of acetic acid than unprotonated ones. Compared with inorganic acid, PAIL had less ability to protonate alcohols. Accordingly, the alcohols in PAIL were more likely to attack protonated carbonyl of acetic acid than that in inorganic acid, and the reaction was accelerated.

Another important point was that the ester products formed a distinct phase because of the polarity difference. However, most water formed from the reaction was dissolved in the PAIL phase. Thus the two kinds of product, ester and water were separated into two phases, and the equilibrium of esterification moved to product formation (Scheme 2). As a result, excellent conversion ratio was achieved.

4. Conclusion

In summary, protophilic amide ionic liquid (PAIL), as the catalyst for the esterification of acetic acid with alcohol, has several advantages: (1) it shows a superior catalytic activity. (2) The separation of the ester product from the reaction phase is rather convenient. (3) The product is of high purity. PAIL shows a unique reaction mechanism: by stabilizing the protonated acetic acid and limiting the alcohol protonation, PAIL accelerates the reaction. The ester forms a separate phase, and the reaction shifts to more product formation to achieve higher conversion.

Acknowledgement

The authors are grateful to NKTRDP (Grant No. 2006BAE01A07-5) for the financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.03.003.

References

[1] R.C. Larock (Ed.), Comprehensive Organic Transformations, second ed., VCH, New York, 1999.
[2] M. Mäki-Arfela, T. Salmi, M. Sundell, K. Ekman, R. Peltonen, J. Lehtonen, Appl. Catal. A: Gen. 184 (1999) 25–32.
[3] A.S.Y. Lee, H.C. Yang, F.Y. Su, Tetrahedron Lett. 42 (2001) 301–303.
[4] P. Mäki-Arfela, T. Salmi, M. Sundell, K. Ekman, R. Peltonen, J. Lehtonen, Appl. Catal. A 184 (1999) 25–32.
[5] T. Welton, Chem. Rev. 99 (1999) 2071–2083.
[6] R. Sheldon, Chem. Commun. 23 (2001) 2399–2407.
[7] C.M. Gordon, Appl. Catal. A: Gen. 222 (2001) 101–117.
[8] D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157–189.
[9] H. Zhao, S.V. Malhotra, Aldrichim. Acta 35 (2002) 75–83.
[10] P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003.
[11] Y. Deng, F. Shi, J. Peng, K. Qiao, J. Mol. Catal. A: Chem. 165 (2001) 33–36.
[12] H. Zhu, F. Yang, J. Tang, M. He, Green Chem. 5 (2003) 38–39.
[13] D.C. Forbes, K.J. Weaver, J. Mol. Catal. A: Chem. 214 (2004) 129–132.
[14] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weave, D.C. Forbes, J.H. Davis, J. Am. Chem. Soc. 124 (2002) 5962–5963.
[15] K. Qiao, C. Yokoyama, Chem. Lett. 33 (2004) 472–473.
[16] J.H. Davis Jr., Chem. Lett. 33 (2004) 1072–1077.
[17] H. Zhang, F. Xu, X. Zhou, G. Zhang, C. Wang, Green Chem. 9 (2007) 1208–1211.
[18] J. Huang, G.A. Baker, H. Luo, K. Hong, Q. Li, N.J. Bjerrum, S. Dai, Green Chem. 8 (2006) 599–602.